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Work on several electronic ceramic materials was conducted during this project. These materials included LiZn Ferrites, PTCR $BaTiO_3$, and Strontium Barium Niobate based ceramics. The main focus of this research was on the study of reliability and reproducibility as a function of processing conditions. More specifically, novel processing techniques, such as sol-gel powder fabrication and powder coating, and processing variables were studied to gain an understanding of the reliability and reproducibility of the above materials.

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RELIABILITY AND REPRODUCIBILITY ACHIEVED VIA GRAIN BOUNDARY ENGINEERING OF HIGH PERFORMANCE ELECTRONIC CERAMICS

FINAL REPORT

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1/31/96

U.S. ARMY RESEARCH OFFICE

DAALO3-91-G-0036

NEW YORK STATE COLLEGE OF CERAMICS

ALFRED UNIVERSITY

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Reliability & Reproducibility Achieved via Grain Boundary Engineering of High Performance Electronic Ceramics

Work on several electronic ceramic materials was conducted during this project. These materials included LiZn Ferrites, PTCR $BaTiO_3$, and Strontium Barium Niobate based ceramics. The main focus of this research was on the study of reliability and reproducibility as a function of processing conditions. More specifically, novel processing techniques, such as sol-gel powder fabrication and powder coating, and processing varriables were studied to gain an understanding of the reliability and reproducibility of the above materials. A breif description of each reserach area follows.

LiZn Ferrites

Effect of Bi_2O_3 on Impurity Ion Distribution and Electrical Resistivity of LiZn Ferrites.;Keith G. Brooks, Yolande Berta and Vasantha R.W. Amarakoon

Preventing the incorporation of impurities in Li-Zn ferrite grains during sintering is essential for production of ceramics with reproducible magnetic and electrical properties. Li-Zn ferrites of composition $Li_{0.3}Zn_{0.4}Mn_{0.05}Fe_{2.25}O_4$ were prepared with sol-gel Bi_2O_3 and borosilicate coatings for sintering aids. The distribution of impurity ions in the sintered ferrites was investigated using transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy (EDS). Ceramics prepared with Bi_2O_3 contained Si, Ca and S impurities, located at the grain boundaries and triple point regions. The low viscosity and good wetting properties of the Bi_2O_3 and to lesser extent the borosilicate liquid phase allowed impurities to be selectively removed from the growing ferrite phase during sintering, thus improving sample resistivies.

Lithium Niobate

Characterization of Sol-Gel Synthesis of Lithium Niobate Powders; Oscar Hernandez, Dana Partis

Lithium niobate powders were synthesized through the gelation of organometalic species of lithium and niobium. Single phase $LiNbO_3$ was successfully formed through calcination of the gelation product. The powders were characterized using FTIR spectroscopy at various stages of the thermal treatment. The FTIR spectra obtained was in good agreement with spectra for $LiNbO_3$ published in literature (characteristic broad band from 300-900 cm^{-1}). These powders were characterized by x-ray diffraction, SEM, and thermal analysis (DTA,TGA). The undergraduate student supported by this project completed his senior thesis and presented his work at a seminar for honors

within the Ceramic Engineering department. These results were also presented at the American Ceramic Society annual meeting in April 1992.

PTCR Thermistors:

Brian LaCourse defended his Masters Thesis, *The Effect of Processing Variables on the Reproducibility of PTCR $BaTiO_3$,* on January 29th, 1993. Much of the results were presented at the 94th and 95th annual American Ceramic Society conventions and have published in the American Ceramic Society Journal.

David Gough, who was partially supported by ARO contract, defended his M.S. thesis entitled "The PTCR Effect in $BaTiO_3$: Processing via Sol-Gel Coating and Characterization of Degradation Behavior," on July 5th, 1993

<u>Processing of $BaTiO_3$</u>; Brian LaCourse, Oscar Hernandez

A tremendous amount of work was done in the area of processing PTCR and dielectric $BaTiO_3$. A low pH, Alkoxide-Hydroxide sol-gel technique was developed by Brian LaCourse and Oscar Hernandez, which was successful in preparing very fine (~80nm) cubic $BaTiO_3$ powder at 600°C. The advantages of the new technique are low processing temperature, less burnoff, improved donor dopant distribution, improved control of the stoichoimetry and microstructure, and comparably low cost. The alkoxide-hydroxide sol-gel technique has been applied to preparing $Ba_{0.66}Sr_{0.34}TiO_3$ and PZT powder with similar success.

The effect of liquid phase composition and distribution on the electrical and microstructural behavior in PTCR $BaTiO_3$ was studied in detail. Common liquid phase additivies are excess TiO_2 and SiO_2. The distribution of the liquid phase during sintering was found to greatly effect the development of the microstructure and the PTCR effect. Pellets with TiO_2 excess as the only liquid phase exhibited poor liquid phase distribution and a duplex microstructure. A more uniform distribution of the liquid phase in the pellets was achieved by prefiring the powder to 1400° C before pressing and sintering the pellets. The improved liquid phase distribution resulted in a more uniform grain size and in an increase in the concentration of grain boundary chemisorbed oxygen. The increase in the grain boundary oxygen concentration increased the acceptor state density which sharpened the PTCR jump. The prefiring step used in this study, to predistribute the liquid phase before sintering, had a very significant effect on the concentration of grain boundary oxygen and on the PTCR behavior, a larger effect than expected.

The addition of SiO_2 to $BaTiO_3$ composition with excess TiO_2 also has been known to improve the liquid phase distribution and the microstructure of PTCR $BaTiO_3$. Because of the dramatic differences in microstructure between $BaTiO_3$ with only excess TiO_2 liquid phase, typically exaggerated grain growth, and with the addition of SiO_2 it has been difficult to determine the effect SiO_2 has on the electrical behavior. During a study $BaTiO_3$ powder with excess TiO_2 and varying amounts of SiO_2, were prefired to 1400^{o}C to ensure that each sample displayed a uniform microstructure. Comparing samples with uniform microstructures enables conclusions to be drawn on the effect of SiO_2 additions on the electrical behavior. It was found that the addition of silica to TiO_2 excess compositions altered the make up of the intergranular phase(s) and the concentration of the grain boundary oxygen. In TiO_2 excess compositions, the intergranular phase was an amorphous, Ti-rich phase most likely 1BaO-3TiO_2. In the compositions containing both TiO_2 excess and SiO_2 there were two distinct intergranular phases. A crystalline Ba/Si rich phase formed along with the Ti-rich phase. The Ba/Si phase was identified as fresnoite, $Ba_2TiSi_2O_8$. The grain size increased with increased silica concentrations due to higher amount of liquid phase sintering. The concentration of grain boundary oxygens, the source of the acceptor states responsible for the grain boundary potential barrier, decreased with increased concentrations of silica. The lower concentration of grain boundary oxygen was a result of either the larger grain size or due to a decrease in oxygen diffusion rate in the higher silica containing samples.

Degradation and Reliability of PTCR $BaTiO_3$; Brian LaCourse, David Gough

It has been known for some time that PTCR material's electrical properties degrade while exposed to a reducing environment such as vacuum, or low partial pressure of oxygen atmosphere. The degradation of the electrical properties is due to the loss of grain boundary oxygen which are the acceptor states responsible for the PTCR properties. Recently devices have been shown to degrade despite not encountering a reducing environment. It has been proposed by our research group that these devices may be degrading as a result of the applied voltage. Research was carried out by Brian LaCourse and three undergrads Todd Stefanik, Anil Jain and Tom Sanborn. In this study PTCR devices were fabricated using the sol-gel technology developed earlier under the current ARO project. First the electrical properties of the devices were tested. The samples were then placed under an applied voltage for a prolong period of time and the electrical properties are subsequently tested. The voltage and time under load were been varied. This study was aimed toward learning more about the reliability of PTCR devices under an applied load and to study additives and processing conditions which improve the reliability of the PTCR properties.

LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED

"Reliability and Reproducibility of Ceramic Sensors: Part I, NTC Thermistors," By James G. Fagan and Vasantha R.W. Amarakoon. Am. Ceram. Soc. Bull. **72** (2) 69-76 (1993).

"Reliability and Reproducibility of Ceramic Sensors: Part II, PTC Thermistors," By James G. Fagan and Vasantha R.W. Amarakoon. Am. Ceram. Soc. Bull. **72** (2) 69-76 (1993).

"Reliability and Reproducibility of Ceramic Sensors: Part III, Humidity Sensors," By James G. Fagan and Vasantha R.W. Amarakoon. Am. Ceram. Soc. Bull. **72** (3) 99-129 (1993).

"Characterization of the Firing Schedule of PTCR $BaTiO_3$," By Brian C. LaCourse and Vasantha R. W. Amarakoon. J. Am. Ceram. Soc. **78** [12] 3352-56 (1995)

"Effect of High Temperature Calcination on the Properties of PTCR $BaTiO_3$," By Brian C. LaCourse and Vasantha R. W. Amarakoon. Submitted to Journal of Materials Research (1993).

Vasantha R.W. Amarakoon and Brian C. LaCourse,"Automotive Sensors;" Encyclopedia of Advanced Materials, Pergamon Press Ltd., Oxford, UK (1994).

Brian C. LaCourse, Oscar Hernandez, and Vasantha R. W. Amarakoon, "Low Cost Sol-gel Processing of Titanate Electronic Ceramic Powders"; in Electronic Materials and Processes for a Peace Time world, International SAMPE Electronics Conference Series, Vol. 7, 1994.

V.R.W. Amarakoon, B. C. LaCourse, J. G. Fagan, J. Pietras, Oscar Hernandez, and J. Peterson, "Thermistors: Fundamentals and Manufacturing Issues", published in the symposia publication, American Ceramic Soc. May 1994.

Brain C. LaCourse, Oscar Hernandez, and Vasantha Amarakoon, "PTCR Thermistors: Reproducibility Achived via Sol-Gel Synthesis", submitted to Sensor publication, conference on automotive sensors, Sept. 20, 1994, Cleveland, Ohio."

Degrees Awarded to Graduate Students Supported by Project:

Brian C. LaCourse............ PTCR Thermistors
M.S. Ceramic Eng. Jan. 1993
Ph.D Ceramic Eng. May 1996

David G. Gough................. Characterization of PTCR Thermistors
M.S. Ceramic Eng. Aug. 1993

Keith G. Brooks........... Lithium Zinc Ferrites
Ph.D. Ceramic Eng. May 1991

Undergraduate Students Related to the Research Area:

Todd Stefanik..................... Reliability of PTCR Thermistors
B.S. Ceramic Eng. May 1995

Anil Jain.............................. Reliability of PTCR Thermistors
B.S. Ceramic Eng. May 1995

Elijah Underhill................. High temperature PTCR Thermistors
B.S. Ceramic Eng. May 1995

Brian Bohlin Sol-Gel Synthesis of Senors
B.S. Ceramic Eng. Jan. 1993

Dana Partis....................... Sol-Gel Synthesis of PTCR Thermistors
B.S. Ceramic Eng. May 1993

Jeff Peterson..................... Processing of Microwave Dielectrics.
B.S. Ceramic Eng. May 1993

David Wright..................... Sol-Gel Coating of LiZn Ferrite Powders
B.S. Ceramic Eng. May 1993

Dean Vernacatola........... FTIR & Raman Spectroscopy of sòl-gel processed electronic ceramic powders.
B.S. Ceramic Eng. Jan. 1992

Rob Cornell................ Processing of PTCR Thermistors
B.S. Ceramic Eng. May 1992

Jason Amaral Processing of electronic ceramics by sol-gel method
B.S. Ceramic Eng. May 1992

VISITS

Several members of the faculty of the New York State Colllege of Ceramics at Alfred University and John Prater gathered for a visit to the US Army Electronics Technology and Devices Labaratory in Fort Monmouth, New Jersey on July 8th, 1992. The vist included a tour of the facilities and several informational seminars. The faculty members included Dean J.W. McCauley, Dr. R. Snyder, Dr. W. Schultze, Dr. Amarakoon, and Dr. A. Clare.

Dr. John Prater visited the New York College of Ceramics at Alfred University on May 27th, 1993. The visit included meetings with Dr. Spriggs on the activities of the Center for Advanced Ceramic Technology (CACT) at Alfred University and with Dean McCauley. Also during the visit a presentation of the projects activities was given by Dr. Amarakoon and several graduate students.

INDUSTRIAL PARTNERSHIPS: Technology Transfer.

Electro-Magnetic Sciences, Norcross, Ga.

LiZn Ferrite

Sol-gel coated LiZn ferrite powder were fabricated at Electro-Magnetic Sciences (dry pressing, sintering, magnetic property measurements). The microstructure of the sintered samples were evaluated at the New York State College of Ceramics at Alfred University in order to determine the suitability of the coating process for industrial manufacturing.

YI Garnets

Sol-gel coating was also adopted to incorporate MnO_2 additives onto the surfaces of YI Garnet powders in order to determine the effect of MnO_2 on the magneto-strictive behavior of YIG.

Texas Instruments Inc., Dallas, Tx.

Texas Instruments Inc. have agreed to test the suitability of sol-gel synthesis of $Ba_{.66}Sr_{.34}TiO_3$ for application in the fabrication of IR sensing night vision devices. $Ba_{.66}Sr_{.34}TiO_3$ ceramics fabricated using the novel sol-gel synthesis developed under ARO sponsorship with graduate students Brian LaCourse, Oscar Hernandez and Jeff Peterson will be tested at Texas Instruments. Microstructure and property measurements will be carried out at Texas Instruments and Alfred University.

Driver-Harris Co., Harrison, NJ.

Driver-Harris has agreed to test the suitability of new PTCR ceramic compositions for application as ceramic space heaters. After lab-scale experiments are completed at the NYS College of Ceramics the materials and devices will be fabricated on a larger scale to test the suitability for commercial production. Driver-Harris Co. which presently manufactures metal based heaters for the consumer market all over the world will conduct a market feasibility test as well.

Quality Components Inc., St. Marys, Pa.

A project was started with a small company in Pennsylvania, who presently makes inductors and capacitors for the American Electronics Industry. This project involves the development of an internal boundary layer capacitor (IBLC) based on $YBa_2Cu_3O_{7-d}$ superconductors for use in high frequency applications. The present titanate based IBLCs can not be used above 10^6 Hz frequencies due to the relaxation of the space charge polarization mechanisms.

Hi-Tech Ceramics, Alfred, NY

A project was started with a small nearby company, Hi-Tech Ceramics, Inc., for the development of porous, reticulated ceramic PTCR heaters and humidity sensors. The project is supported with matching funds from the New York Center for Advanced Ceramic Technology (CACT) at Alfred University. Matching support includes $26,000 for the support of a graduate student (James Fagan) and undergraduate student (Brian Bohlin) from the CACT and support for materials, supplies, etc. from Hi-Tech Ceramics. Work in the development of PTCR $BaTiO_3$ supported by ARO will be used to some extent for this project on porous ceramic heaters and humidity sensors. Results of this work will be used by Hi-Tech ceramics to develop new product lines.